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# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO STABILISERS FOR PROPELLANTS

I, Secretary of State for Defence, London, do hereby declare the invention for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to novel stabilisers for use in composite-modified double-base propellants and to propellants containing them.

It is known that double-base propellants, that is propellants containing nitrocellulose and a liquid nitrate ester or a mixture of liquid nitrate esters, require a small proportion of stabiliser in order to permit long-term storage. In the absence of the stabiliser, the propellant compositions slowly become acidic due to decomposition of the nitrate esters. This acidity catalyses further decomposition resulting in a degradation of mechanical and ballistic properties and even a dangerous degree of self-heating which may lead to a disastrous ignition.

A small amount of chalk or similar mild alkali is used in the nitro-cellulose during its stabilisation prior to mixing with the other propellant ingredients and is included, therefore, amongst conventional stabilisers. In addition, an organic substance or mixture of substances, including substituted ureas such as diethyl diphenyl urea (carbamite), urethanes such as methyl phenyl urethane, or nitrodiphenylamine (NDPA) are used in proportions up to about 3%. Diphenylamine may be used at low nitroglycerine contents (up to about 15 per cent nitroglycerine). Higher proportions of stabilisers may be used to improve plasticisation or to moderate ballistic properties but these higher proportions are not normally required for stabilisation as such.

Other ingredients, such as a fuel and/or a source of oxygen, for instance a metal powder and/or ammonium perchlorate, may be added to double-base propellants to modify specific properties such as energy release. These propellants are known as composite-modified double-base propellants (CMDB). The stability of these propellants when modified to include ammonium perchlorate is, however, unacceptable even when the heretofore mentioned stabilisers are used. As used in this specification the expression

composite-modified double-base propellant (CMDB) refers to those propellants which include ammonium perchlorate as an essential ingredient.

The life of a propellant may be assessed by different criteria as, for instance, its chemical stability which may be a main factor in its safety characteristics or its physical stability which in general determines the continuance of its ballistic properties. The effective life is, of necessity, determined by the shortest time given by any of these criteria. In the case of composite-modified double-base propellants, the principal reasons for unacceptable stability have been (1) the poor stability as shown by the flammability and cracking tests and (2) a low total stabilising capacity as shown by the flammability test.

Acceptable stability of CMDB propellants is not automatically attained by a simple increase in the proportion of the conventional stabiliser present. These stabilisers act by combining with the oxides of nitrogen produced by the decomposition of the nitrate esters and do not of necessity react with the breakdown products of ammonium perchlorate and other oxidising agents. There is, in addition, a limited solubility of these stabilisers in the propellant matrix as evidenced by 'blooming' on storage. Also an excess of stabiliser detracts from the energy of the propellant.

It has now been found that composite-modified double-base propellants may be successfully stabilised to permit long-term storage by using a stabiliser comprising a mixture of any known stabiliser for double-base propellants and at least two of the compounds nitroguanidine, para-nitro-N-methyl aniline, and an inorganic compound as hereinafter defined.

The inorganic compound for use in the invention is defined as a basic compound which reacts with strong acids but is not sufficiently basic to react directly with the other ingredients, particularly ammonium perchlorate or the nitrate esters, to any significant extent. It will not react with the other ingredients to form sensitive metallic salts nor act as a decomposition catalyst for the nitrate esters.

According to the invention, there is provided a stabiliser for use in composite-modified

double-base propellants comprising a mixture of at least three compounds of any known stabiliser for propellants and at least two of the compounds nitroguanidine, para-nitro-N-methyl aniline, and an inorganic compound as hereinbefore defined.

- 5 Preferably, the stabiliser mixture contains all three of the compounds nitroguanidine, para-nitro-N-methyl aniline and an inorganic compound in addition to the known stabiliser or stabilisers.

The use of nitroguanidine has the advantage that it is self-energetic and as a consequence much larger quantities of it may be used than is normal for conventional stabilisers.

- 15 Preferably, the inorganic compound is lead carbonate or a basic lead carbonate.

Stabilisers known to the art may include diphenylamine, 2-nitrodiphenylamine, diethyl diphenyl urea, p-nitro-N-methyl aniline and methyl phenyl urethane.

- 20 The invention also provides novel composite-modified double-base propellants containing the mixture of stabilisers as hereinbefore described.

The novel propellants contain nitro-cellulose within the range 14% to 35%, at least one nitrate ester, such as nitro-glycerine, diethylene glycol dinitrate, triethylene glycol dinitrate or trimethylol ethane trinitrate within the range 25% to 40%, a non-explosive desensitiser such as an ester, for example dimethyl phthalates or triacetin, within the range up to 8%, an oxidising agent consisting at least in part of ammonium perchlorate within the range 5% to 50%, a fuel such as aluminium powder within the range up to 25% and a mixture of stabilisers within the range 2.5% to 10%. All percentages are by weight.

- 40 Preferably the non-explosive desensitiser is a phthalate ester. It has been found that triacetin in the presence of ammonium perchlorate whilst giving compositions having an acceptable stability, tends to enhance the development of acidity on storage.

- 45 The effectiveness of stabilisers in propellants is usually confirmed by storage trials at elevated temperatures whereby the rate of decomposition is accelerated and the effective life of the propellant at ambient temperatures may be determined relatively quickly. The life of the propellant may be affected by a reduction in the amount of stabiliser due to nitration or nitrosation of the stabiliser by oxides of nitrogen produced by decomposition of the nitrate esters or more usually by a physical deterioration (cracking) due to the evolution of small amounts of gases including permanent gases as for instance nitrogen. Conventional known stabilisers allow the propellant to generate gases

- 60 on hot-storage-including the permanent gases which are not very soluble in the propellant, and which diffuse away very slowly. When the thickness of the propellant is large and/or its

temperature is too high, the gas evolved may cause fissures in the propellant creating extra burning surfaces and affecting the internal ballistics.

A series of CMDB propellants were prepared to the following composition: nitrocellulose (12.6%N) 22.0%; nitroglycerines 28.9%; ammonium perchlorate, 24.7%; aluminium, 16.4%; and triacetin, 7.0%. All percentages are by weight.

To these, varying proportions of the novel stabiliser system, nitroguanidine (picrite), a basic lead carbonate (WL), and para-nitro N-methylaniline (NMA) were added in addition to a known stabiliser, 2-nitro diphenylamine (NDPA) and the prepared propellants were subjected to hot storage trials, using as controls propellants made to the above composition containing 1.0 per cent of NDPA and others containing about 4 per cent of mixtures of NPA and NMA. In one of the novel prepared propellants (Sample 4) the triacetin was replaced by dimethyl phthalate and in another. (Sample 6), the nitroglycerine and triacetin were replaced by diethylene glycol dinitrate.

The initial stabiliser content of the propellants and the effect of storage at varying temperatures is given in Table 1.

Tests carried out include an X-ray examination for the appearance of cracks followed by a destructive visual examination, and a flammability test in which cubes of the propellant, wrapped in aluminium foil, were stored in loosely plugged stainless-steel tubes heated to 95°C until ignition occurred, when the plugs were ejected.

The prepared propellants were also stored at 80°C and analyses were carried out at regular intervals to determine the percentage of residual NDPA and NMA. These results are given in Table 2. Similar results obtained from larger charges stored at 60°C are given in Table 3. Owing to analytical difficulties, the percentages of WL and picrite are not given.

In all cases, the novel propellants according to the invention had much greater stability and freedom from physical defects than the control propellants.

Sample No 6 containing the combination of NDPA, NMA, basic lead carbonate and nitroguanidine with diethylene glycol dinitrate was outstanding and Sample No 4 containing dimethyl phthalate as the plasticiser was excellent.

What we claim is:-

1. A stabiliser for use in composite-modified double-base propellants comprising a mixture of at least three components including any known stabiliser for propellants and at least two of the compounds nitroguanidine, para-nitro-N-methyl aniline and an inorganic compound as hereinbefore defined.

2. A stabiliser according to Claim 1 comprising a mixture of any known stabiliser for propellants and nitroguanidines para-nitro-N-methyl aniline, and an inorganic compound as hereinbefore defined. 25
- 5 3. A stabiliser according to Claim 1 or Claim 2 wherein the inorganic compound is lead carbonate or a basic lead carbonate.
- 10 4. A stabiliser according to any one of Claims 1 to 3 wherein the known stabiliser is at least one of the compounds, diphenylamine, 2-nitro diphenylamine, diethyl diphenyl urea, p-nitro-N-methyl aniline, and methyl phenyl urethane. 30
- 15 5. A composite-modified double-base propellant incorporating at least in part a stabiliser according to any one of Claims 1 to 4 comprising nitrocellulose within the range 14 per cent to 35 per cent by weight, at least one 35 nitrate ester within the range 25 per cent to 40 per cent by weight, a non-explosive desensitiser within the range up to 8 per cent by weight, an oxidising agent consisting at least in part of ammonium perchlorate in the range 5 to 50 per cent by weight, a fuel within the range up to 25 per cent by weight and a mixture of stabilisers within the range 2.5 per cent to 10 per cent. 45
6. A composite-modified double-base propellant according to Claim 5 wherein the nitrate ester is nitro-glycerine, diethylene glycol dinitrate, triethylene glycol dinitrate or trimethylol ethane trinitrate.
7. A composite-modified double-base propellant according to Claim 5 or Claim 6 wherein the non-explosive desensitiser is an ester. 35
8. A composite-modified double-base propellant according to Claim 7 wherein the ester is dimethyl phthalate or triacetin.
9. A composite-modified double-base propellant according to any one of Claims 5 to 8 wherein the fuel is aluminium powder. 40
10. A composite-modified double-base propellant according to Claim 5 substantially as described in the specification. 45

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Table 1  
Effect on Thermal Stability and Cracking

Sample No.	Stabilizers (per cent)				Cracking Life		
	HDPE	HMA	WL	Pke, $f_{max}$	12.7 cm Cubes Firing times at 950°C (hr)	50 mm. Cubes at 80°C (days)	150 mm cylinders at 60°C (weeks)
1	0.3	1.1	0.35	2.15	245	13	14
2	1.0	0.35	H11	2.10	154, 190	6	26
3	1.0	1.1	0.35	H11	117, 135	16	21*
4	1.0	0.35	0.35	2.15	> 216	20	29
5	1.0	0.35	0.35	2.10	> 216	13	43
6	1.0	0.35	0.35	2.20	> 216	34	> 52
7	0.7	-	-	-	-	1	-
8	1.0	-	-	-	30	1-3	-
9	1.0	-	-	-	46	1-2	-
10	1.0	-	-	-	38	1-2 (50 mm cylinder)	-
11	3.0	0.8	-	-	89, 76	0-1	14-21
12	0.85	3.0	-	-	89, 81	0-1	14-21

\*Plays were discrete bubbles and not usual gas cracking flaws

Storage time (weeks)	Sample 7	Sample 8	Sample 9	Sample 11	Sample 12	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA	ADPA
0	0.7	1.0	1.0	0.6	3.0	3.0	0.95	1.0	0.29	0.35	1.0
1	0.37	(8.5)	0.56	(3.3)	1.84	1.84	0.65	0.75	0.26	0.02	0.50
2	-	days	-	days	days	days	-	0.56	0.29	0.07	0.44
3	-	-	-	-	-	-	-	0.56	0.29	0.07	0.44
4	-	-	-	-	-	-	-	0.10	0.15	0.04	0.12
5	-	-	-	-	-	-	-	0.08	0.24	0.12	0.23
6	-	-	-	-	-	-	-	0.09	0.11	0.09	0.09
7	-	-	-	-	-	-	-	0.09	0.11	0.09	0.09

Table 3  
Percentages Residual Strain after at 600°C on 150 mm diameter Solid Chromite

Storage Time (weeks)	Sample 11		Sample 12		Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
	NDPA	NTA	NDPA	NTA	NDPA	NTA	NDPA	NTA	NDPA	NTA	NDPA	NTA	NDPA	NTA	NDPA	NTA
0	3.0 1.67 (21 days)	0.8 0.77 (21 days)	0.05 0.53 (21 days)	3.0 2.82 (21 days)	0.30 0.31	1.1 0.77	1.0 0.91	0.35 0.10	0.98 0.94	1.0 0.73	1.0 0.35	1.0 0.35	1.0 0.35	1.0 0.35	1.0 0.35	0.35
13	-	-	-	-	-	-	-	-	0.91 0.62 (21 weeks) Not specified	-	-	-	-	-	-	-
23	-	-	-	-	0.25	0.57	0.65 0.05 (27 weeks)	-	-	-	-	-	-	-	-	-
26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
39	-	-	-	-	0.24	0.44	-	-	-	-	-	-	-	-	-	-
40	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
48	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
52	-	-	-	-	0.24	0.25	0.54 0.05	0.78 0.32	-	-	-	-	-	-	-	-
60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-